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COMPLETE SPECIFICATION

A Crystalline or Vitreous-Crystalline Devitrified Glass having a Negative or very low and positive Thermal Expansion Coefficient

We, SIEMENS-SCHUCKERTWERKE AKTIEN-GESELLSCHAFT, a German Company, of Berlin and Erlangen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

We, in Germany, are aware of a proposal to utilise the tendency of glasses to devitrify at relatively high temperatures in the production of crystalline or vitreous-crystalline ceramic-like materials. If a glass is maintained at its devitrification temperature for some time, it is converted into a crystalline or vitreous crystalline state. In the devitrification, crystals are formed from the components of the glass. Depending upon the composition of the glass and the manner in which the devitrification is controlled, the end product may be either completely crystalline or may to some extent still contain a glass phase.

According to one aspect of the present invention there is provided a crystalline or vitreous-crystalline ceramic-like material which has been prepared by devitrifying glass by heat treatment and which has a coefficient of thermal expansion which is either negative or is very low and positive, said material consisting predominantly (i.e. in a proportion of at least 50% by weight) of beta - eucryptite as devitrification product.

According to another aspect of the present invention there is provided a process for producing a crystalline or vitreous-crystalline ceramic-like material having a coefficient of thermal expansion which is either negative or is very low and positive, wherein a glass containing the components of beta - eucryptite is devitrified by thermal treatment and the product consists predominantly (i.e. in a proportion of at least 50% by weight) of beta-eucryptite as devitrification product.

The ceramic-like material can well withstand temperature fluctuations and it has high mechanical strength as compared with materials produced in accordance with the prior proposal mentioned above. For certain applications, a devitrification product is favourable which contains magnesium titanate as well as β - eucryptite. The ceramic-like material may, with advantage, contain a proportion of at least 60% by weight of beta-eucryptite.

In producing the ceramic-like material by devitrifying by thermal treatment a glass containing the components of beta - eucryptite, there may be added to the initial components of the glass, for forming magnesium titanate in the devitrification product, MgO and TiO_2 , in the proportion of from 0.5% to 10% by weight of TiO_2 , preferably 5% by weight, and from 1% to 20% by weight of MgO, preferably 10% by weight.

A generally applicable rule affecting the choice of the temperature for carrying out the devitrification is that it must naturally be above the lower devitrification temperature in the sense in which this term is employed in glass technology. The higher the temperature is above this level, the more rapidly does the devitrification process take place. On the other hand, the degree of devitrification may also be influenced by the choice of the period of treatment at the temperature chosen. The number and the size of the crystals formed in the devitrification and thus the mechanical, thermal and electrical properties of the material can be considerably influenced by variation of the treatment temperature and the period of treatment. If a treatment temperature of 1200°C. is chosen, a complete devitrification of the starting material is obtained within 1 hour.

It is known to employ additions of boric acid in the materials for making glass in

order to improve their fusibility. Such additions reduce the toughness of the melt at higher temperatures and increase it at low temperatures. Boric acid may also be utilised in the process now proposed, in order to effect a considerable lowering of the devitrification temperature. A considerable advantage is thereby obtained in the technical performance of the devitrification process: at relatively low temperatures (temperatures in the neighbourhood of the softening point), the free mobility of the individual molecules is hindered and the formation of crystallisation centres is promoted. Owing to the increased toughness of the glass at low temperature, the linear crystallisation speed is reduced. At a low linear crystallisation speed and with a high spontaneous crystallisation capacity, the entire glass mass is permeated by minute crystals. This is very important to the homogeneity of the end

product. The proportion of boric acid included in the materials for making the glass may be such that the glass contains between 1 and 8%, preferably 4%, by weight, of B_2O_3 . The boric acid may be included in the materials for making the glass, with the components of beta-eucryptite and with or without the MgO and TiO_2 .

In addition, use may be made of the fact that if a quantity of TiO_2 is present it greatly reduces the thermal contraction of beta-eucryptite, while the addition of MgO in the presence of TiO_2 partially compensates for this effect. By an appropriate choice of the TiO_2 and MgO additions, therefore, the thermal expansion behaviour can be adjusted as desired within a certain range. In the table, the thermal expansion coefficients (α) of a number of the ceramic-like materials containing beta-eucryptite are given.

TABLE

Number of the glass specimens		1	2	3	4	5	6	7
Composition of the glass in % by weight	SiO_2	46.8	46.8	41.6	46.8	48.8	46.8	44.9
	Al_2O_3	33.7	33.7	29.9	33.7	35.1	33.7	32.3
	Li_2O	11.2	2.8	6.3	7.1	3.0	7.1	6.8
	TiO_2	4.2	4.2	7.4	4.2	4.4	8.3	4.0
	MgO	4.1	12.5	14.8	8.2	8.7	4.1	12.0
Devitrification temperature (1 hour) ($^{\circ}C.$)		1200	1200	1000	1000	1200	1000	1100
Thermal Expansion Coefficient ($\alpha \cdot 10^7$, $^{\circ}C.$)								
20° to x° C.		600° -24	400° 0	320° 7	220° 5			
20° to 800° C.			5	14	26	21	23	36

Specimens Nos. 2, 3 and 4 show that it is possible with the material now proposed to produce over a range of a few hundred degrees C. a substantially infinitesimal coefficient of thermal expansion similar to that of quartz. This is important when using bodies made of the material in question in many branches of the art, more especially when these bodies are exposed to severe temperature fluctuations. It is also of importance, when parts made of the ceramic-like material are to be connected to metal parts. Thus, for example, it is possible to shrink or solder a screw-threaded metal ring on to a bushing

consisting of a material according to Specimen No. 2 without cracking. These properties afford to the material according to the present proposal numerous possibilities of application in industry, for example in electrical engineering, as a ceramic insulating body, as a pin-type insulator or as a rod-type insulator for valve parts and the like.

The properties of the material now proposed make it suitable for use in devices loaded by high and ultra-high temperature, such as turbines, internal combustion engines and the like.

WHAT WE CLAIM IS:—

1. A crystalline or vitreous-crystalline ceramic-like material which has been prepared by devitrifying glass by heat treatment and which has a coefficient of thermal expansion which is either negative or is very low and positive, said material consisting predominantly (i.e. in a proportion of at least 50% by weight) of beta-eucryptite as devitrification product.
2. A material according to claim 1 and containing magnesium titanate.
3. A material according to claim 1 or 2 having at least 60% by weight of beta-eucryptite.
4. A process for producing a crystalline or vitreous-crystalline ceramic-like material having a coefficient of thermal expansion which is either negative or is very low and positive, wherein a glass containing the components of beta - eucryptite is devitrified by thermal treatment and the product consists predominantly (i.e. in a proportion of at least 50% by weight) of beta - eucryptite as devitrification product.
5. A process according to claim 4, wherein the glass employed also contains MgO and TiO₂.
6. A process according to claim 5, wherein the glass employed contains from 0.5 to 10% by weight of TiO₂ and from 1% to 20% by weight of MgO.
7. A process according to claim 6, wherein the glass employed contains about 5% by weight of TiO₂ and about 10% by weight of MgO.
8. A process according to any one of claims 4 to 7, wherein the glass employed also contains B₂O₃.
9. A process according to claim 8 wherein the proportion of B₂O₃ in the glass is 1 to 8% by weight.
10. A process according to claim 9, wherein the proportion of B₂O₃ in the glass is about 4% by weight.
11. A crystalline or vitreous-crystalline ceramic-like material which has a coefficient of thermal expansion which is either negative or is very low and positive, the material having been prepared by the process according to any one of claims 5 to 7.
12. A crystalline or vitreous-crystalline ceramic-like material substantially as hereinbefore described.
13. A process for producing a crystalline or vitreous crystalline ceramic-like material substantially as hereinbefore described.

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